

STRUCTURAL CHARACTERISTICS AND THERMAL STABILITY OF FGD SCRUBBER SLUDGE

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ABSTRACT

We investigated the structural and thermal properties of flue gas desulfurization (FGD) scrubber sludge (CWLP, Springfield, Illinois) to explore this residue's suitability for conversion into structural materials. The structural characteristics of the sludge were obtained by undertaking transmission-Fourier transform infrared (FTIR), diffuse reflectance-FTIR (DRIFT), and scanning electron microscopy (SEM) measurements, while the thermal stability of the residue was gauged by conducting differential scanning calorimetry (DSC) and differential thermal analysis (DTA) experiments at $30^{\circ}\text{C} < T < 1150^{\circ}\text{C}$. The SEM data and vibrational results suggest that this residue is largely gypsum and contains a few particles of fly ash. We did observe only very weak SO_3^{2-} bands in the sludge's FTIR spectrum. The sludge is primarily composed of two types of crystallites, i.e., rectangular-shaped needles and parallelogram-shaped crystals. The thermal results on the sludge indicate that the water is lost from the sample in a two step process at $150^{\circ}\text{C} < T < 200^{\circ}\text{C}$. The observed dehydration enthalpy of 585 J/g was higher than that reported for gypsum. However, our results are consistent with the commercial gypsum samples we tested. After exothermic transformation at 380°C , the sludge sample and the commercial gypsum samples remained thermally inert at $400^{\circ}\text{C} < T < 1150^{\circ}\text{C}$.

INTRODUCTION

Presently more than 90 million tons of coal combustion byproducts, i.e., fly ashes, bottom ashes, and scrubber sludges, are generated in the U.S. annually. These byproducts' yield is expected to grow in the near future as the Clean Air Act is stringently enforced [1-3]. The Midwestern USA coals are high in sulfur content, and the combustion of these coals results in emissions containing a high percentage of SO_x . Flue gas desulfurization (FGD) technology is commonly used in order to reduce the emission of these venomous gases. Some power plants use a scrubber unit to capture SO_x , and this produces about 20 million tons of scrubber sludge in the USA alone.

It is generally believed that the major components of scrubber sludge, depending upon whether it is a forced oxygen unit, are calcium sulfite (CaSO_3), calcium sulfate (CaSO_4), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). In addition, small amounts of fly ash and excess scrubbing reagents have been reported in the sludges. When lime or limestone is used as a sorbent material in the FGD systems, the purity of calcium sulfate obtained as a byproduct ranges between 95% to 99%. Lime reacts with SO_2 in the scrubber unit, and different products are formed depending on the temperature of the system. It has been reported that only CaSO_3 was formed below 550°C , while a mixture of CaSO_3 , CaSO_4 and CaS was produced at $600^{\circ}\text{C} < T < 850^{\circ}\text{C}$ [4]. Above 800°C , only CaSO_4 and CaS were formed. On the other hand, if CaCO_3 is used in a scrubber unit, different byproducts are formed depending on the temperature at which the flue gases react with it. The reactions of CaCO_3 with air (O_2) + SO_2 have been thoroughly investigated at different temperatures [5]. It was found that the amount of sulfite formed in such a system was always small compared to the other phases. Significant amounts of CaSO_3 were formed only at $T > 600^{\circ}\text{C}$. Formation of CaSO_4 was extremely low but detectable at temperatures above 400°C . At $T \geq 600^{\circ}\text{C}$, the formation of CaSO_3 was significant and reached a maximum at 800°C . Other traces detected above 800°C were CaCO_3 , CaO , CaS , CaSO_3 , and Ca(OH)_2 .

It has been reported that the hydrated calcium sulfate, particularly gypsum, produced as a byproduct of scrubbing flue gases, could be used in a variety of applications. Most of the scrubber sludge produced in the U.S. is currently used only in landfill applications [1-3]. Some other applications of this residue are road construction [6], wallboard manufacturing [7], and agricultural [8]. However, the quantity of these residues produced as well as the cost of disposal are very large and are increasing every year. Hence, it is necessary to develop more applications in which these residues can be utilized. If the gypsum is to be used in different market applications, the fly ash must be removed from the flue gas before the scrubbing process to avoid contamination. Also, it is necessary to ascertain whether scrubber sludges produced are environmentally safe.

We have initiated systematic microscopic, thermal, and spectroscopic measurements on various scrubber sludges produced by different power plants with a view to characterize these byproducts for their suitability in the construction industry. Here we report our results on a sludge which is rich in hydrated calcium sulfate

EXPERIMENTAL TECHNIQUES

The scrubber sludge we examined was from City Water and Light Power Plant (CWLP) in Springfield, Illinois. This power plant combusts Illinois No. 5 and Illinois No. 6 coals. The residue sample was obtained from the sample bank established at the Mining Engineering department of Southern Illinois University at Carbondale. For comparison purposes, we also characterized two gypsum samples, i.e., Satin Spar Gypsum (SSG), and Gypsum Var Alabaster (GVA), obtained from Sargent-Welch. The SEM study of the CWLP scrubber sludge sample was carried out using a Hitachi S570 scanning electron microscope. The thermal characterization of the scrubber sludge and the mineral gypsum samples was carried out using DSC and DTA techniques. In DSC experiments, the samples were subjected to heating in N_2 atmosphere at temperatures $40^\circ C < T < 450^\circ C$ using a well calibrated [9,10] Perkin-Elmer DSC 7 system. A heating rate of $10^\circ C/min$ was used. Aluminum (Al) pans were used to encapsulate the sample with holes drilled in them so that any vapors or gases evolved from the sample could escape easily. The higher temperature ($50^\circ C < T < 1100^\circ C$) thermal behavior of our samples was probed by undertaking DTA measurements using a Perkin-Elmer DTA 7 system. A heating rate of $20^\circ C/min$ was used under N_2 gas environment. We used KBr pellet technique to record FTIR spectra of CWLP sludge and gypsum samples at 4 cm^{-1} resolution. We also conducted *in-situ* diffuse reflectance-FTIR (DRIFT) measurements on CWLP scrubber sludge at $20^\circ C < T < 275^\circ C$. While FTIR spectra were recorded on a IBM IR 44 FTIR spectrometer, the DRIFT spectra were collected on a Nicolet 740 FTIR spectrometer.

RESULTS AND DISCUSSION

A careful examination of SEM microphotographs of CWLP scrubber sludge indicates that the air dried scrubber sludge generally consisted of two distinct morphologies of crystals. In the first morphology, the crystals were parallelogram-shaped, and this shape is typical of gypsum ($CaSO_4 \cdot 2H_2O$) [11]. The second type of morphology exhibited by sludge particles was rectangular-shaped crystals, ranging from 50 to $400\text{ }\mu m$ in length and about $50\text{ }\mu m$ in thickness. These rectangular-shaped crystals (see Fig. 1) showed a random pore structure within the crystallites and thus, will be difficult to dewater. It is worth pointing out that the CWLP scrubber sludge we examined did show a very few particles of fly ash. However, their concentration in the sludge was almost negligible.

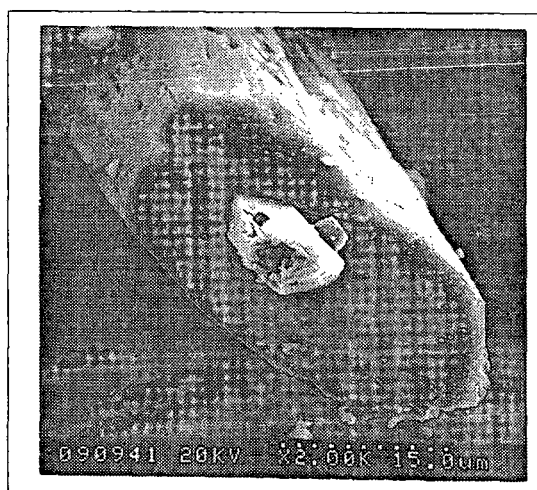


Fig. 1 SEM microphotograph of scrubber sludge crystallites.

Figure 2 depicts DSC thermographs for CWLP scrubber sludge, satin spar gypsum (SSG), and gypsum var alabaster (GVA) samples. The DSC thermograph of CWLP scrubber sludge showed two strong endothermic peaks located at $154^\circ C$ and $189^\circ C$ and a weak exothermic peak at $380^\circ C$. Similar thermal events were also observed for mineral gypsum samples except the peak

temperatures were slightly different. Based on work reported in the literature [12,13], the endothermic peaks can be associated with the loss of water from the sludge. It appears

that the dehydration reaction in our CWLP scrubber sludge sample occurred in two steps, just as it has been reported for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [13]. The peak at 154°C may be due to the loss of 1.5 water molecules which resulted in the formation of hemihydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$. The dehydration further continued when at 189°C , γ -anhydrite was formed by the loss of the remaining 0.5 water molecule. Even though there are some dissimilarities in the peak positions of the observed endothermic and exothermic reactions observed for CWLP scrubber sludge and mineral gypsum samples, we believe the CWLP scrubber sludge is largely composed of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

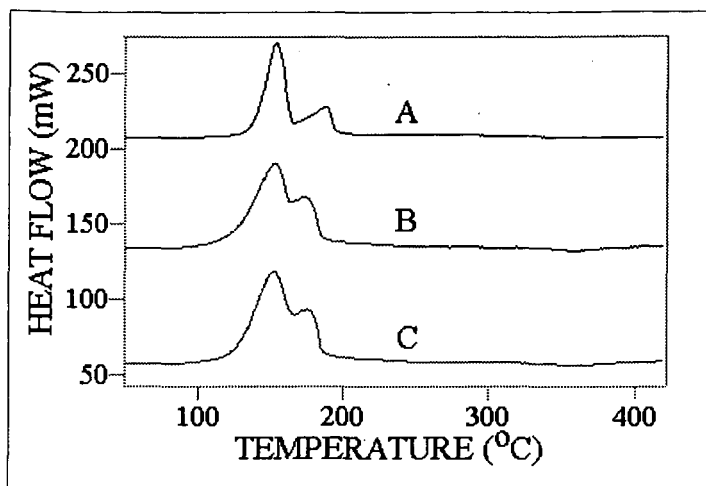


Fig. 2 DSC thermographs of (A) CWLP scrubber sludge, (B) Satin Spar Gypsum (SSG), and (C) Gypsum Var Alabaster (GVA) samples. The two endothermic peaks at $100^\circ\text{C} < T < 200^\circ\text{C}$ represent decomposition and desorption of water from the samples.

Our results indicate that the enthalpy of dehydration reaction for CWLP scrubber sludge was 592 J/g , which is much larger than that reported by Strydom et al. [14] for synthetic gypsum. Strydom et al., using DSC technique, reported that the dehydration enthalpy of synthetic gypsum varied over a range of 377 J/g to 420 J/g . However, DSC experiments conducted on mineral gypsum samples in our laboratory revealed a value of 656 J/g and 704 J/g for GVA and SSG, respectively. Since the observed dehydration enthalpy will be strongly influenced by such factors as packing of the particles in the Al pans, the consistency and uniformity of the holes in the pans, and the ramping rates used, some variation in the enthalpy value is expected. However, to provide conclusive evidence, additional experiments will be needed and are in progress.

Table 1 summarizes our DTA results on scrubber as well as mineral gypsum samples at $50^\circ\text{C} < T < 1100^\circ\text{C}$. Similar to DSC results, the DTA experiments on the sludge exhibited a two-step dehydration reaction. This was followed by a polymorphous transformation, i.e., $\gamma\text{-CaSO}_4$ transforms into $\beta\text{-CaSO}_4$ at 380°C . After the formation of β -anhydrite at 380°C , the DTA results did not show any other thermal event either for sludge or mineral gypsum samples at $380^\circ\text{C} < T < 1100^\circ\text{C}$.

We attempted to ascertain the chemical structure and composition of CWLP scrubber sludge by conducting FTIR spectroscopic measurements. The infrared (IR) frequencies along with the observed peak heights are reproduced in Table 2. Also listed in Table 2 are the IR band frequencies for mineral gypsum samples. The IR spectrum of scrubber sludge showed two vibrational modes at 3615 cm^{-1} (ν_3 stretch of HO-H) and 3557 cm^{-1} (ν_1 stretch of HO-H) in the water's stretching region, while a single oscillator at 1620 cm^{-1} was observed in the water's bending region. On the other hand, the mineral gypsum samples showed three vibrational bands in the water's stretching region and two IR bands in the water's bending region. Bensted and Prakash [15] have suggested that the different phases of calcium sulfate can be distinguished by the vibrational modes of water observed. For example, O-H stretching vibrations are observed at ~ 3555 , ~ 3500 , and $\sim 3400 \text{ cm}^{-1}$ in the water's stretching region for gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) along with two oscillators at ~ 1680 and $\sim 1620 \text{ cm}^{-1}$ in the water's bending region. Hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$)

produces two vibrational bands in the O-H stretching region at around 3610 and 3560 cm^{-1} and a single oscillator in the H-O-H bending region. Since we observed only three vibrational modes of water at $1500 < \text{frequency} < 3800 \text{ cm}^{-1}$ for our scrubber sludge sample, see Table 2, it is reasonable to argue that our sample is largely hemihydrate. This observation is not consistent with our DSC and DTA results which suggested that our CWLP scrubber sludge was mostly gypsum. It is possible that during the formation of KBr pellets and subsequent drying in a desiccator, the gypsum got converted into hemihydrate phase.

TABLE 1
Summary of DTA results on CWLP scrubber sludge and mineral gypsum samples at $50^\circ\text{C} < T < 1100^\circ\text{C}$.

Sample	Peak Begins at ($^\circ\text{C}$)	Peak End at ($^\circ\text{C}$)	Peak Temperatures ($^\circ\text{C}$)	Remark
CWLP Scrubber Sludge	93 335	273 480	165, 181 380	Endothermic Exothermic
Satin Spar Gypsum	64 330	316 480	203 378	Endothermic Exothermic
Gypsum Var Alabaster	97 338	300 432	183, 193 379	Endothermic Exothermic

TABLE 2
The observed infrared bands for CWLP scrubber sludge and mineral gypsum samples. The observed frequencies are in cm^{-1} (value in parentheses is peak height in arbitrary units).

CWLP Scrubber Sludge	Satin Spar Gypsum	Gypsum Var Alabaster	Assignment
3613(0.51)	3545 (0.45)	3548 (0.50)	O-H stretch (ν_3) (H_2O)
3560(0.36)	3494 (0.40)	3497 (0.39)	O-H stretch (ν_1) (H_2O)
	3405 (0.51)	3405 (0.59)	O-H stretch ν_1 (H_2O)
	3243 (0.18)	3243 (0.17)	$2(\nu_2)$ (H_2O)
2361 (0.10)	2240 (0.06)	2240 (0.06)	$2(\nu_3)$ in SO_4
2334 (0.09)	2116 (0.04)	2120 (0.04)	$\nu_1 + \nu_3$ in SO_4
	1687 (0.15)	1686 (0.13)	H-O-H bend (ν_2)
1622 (0.32)	1622 (0.29)	1621 (0.30)	H-O-H bend (ν_2)
1154 (4.27)	1142 (0.95)	1144 (1.1)	ν_3 of SO_4
1126 (1.50)	1116 (0.96)	1117 (1.1)	ν_3 of SO_4
1105 (1.35)			ν_3 of SO_4
1007 (0.18)			ν_1 of SO_4
662 (0.52)	669 (0.31)	669 (0.32)	ν_4 of SO_4
602 (0.50)	602 (0.30)	602 (0.30)	ν_4 of SO_4
	463 (0.05)	461 (0.06)	

We performed *in-situ* DRIFT measurements at $20^\circ\text{C} < T < 260^\circ\text{C}$ on air-dried CWLP scrubber sludge to answer whether this sludge was in gypsum or hemihydrate phase. Figure 3 reproduces how temperature altered the DRIFT spectrum of the sludge. At 30°C the sludge's DRIFT spectrum showed four vibrational bands in the water's stretching region, i.e., at 3556, 3489, 3402, and 3249 cm^{-1} and two bands at 1687 and 1620 cm^{-1} in the water's bending region. As the temperature was raised above 30°C , the band at 3556 cm^{-1} lost intensity and shifted to 3570 cm^{-1} at 106°C . The band at 1687 cm^{-1} rapidly lost intensity at 106°C and disappeared at 135°C . At $135^\circ\text{C} < T < 180^\circ\text{C}$, we observed two bands at 3630 and 3550 cm^{-1} in the O-H stretching region and a single band at around 1624 cm^{-1} in the water's bending region. Above $T > 180^\circ\text{C}$, the H-O-H bands were very weak if they were observed at all. Based on our *in-situ* DRIFT results, we believe CWLP scrubber sludge mostly contains gypsum phase which readily loses water at $50^\circ\text{C} < T <$

135°C to form hemihydrate phase. It transforms into reversible anhydrite phase at 160°C < T < 260°C. The vibrational bands at 1154, 1126, and 1105 cm⁻¹ could be assigned to ν_3 mode of SO₄²⁻ ions of gypsum, while the bands at 662 and 602 cm⁻¹ are due to ν_4 mode of sulfate ions. It is known that SO₃²⁻ ions produce a characteristic band at around 975 cm⁻¹. We did observe a very weak band at 977 cm⁻¹ in our DRIFT spectrum, suggesting that CWLP does contain a very small quantity of CaSO₃.

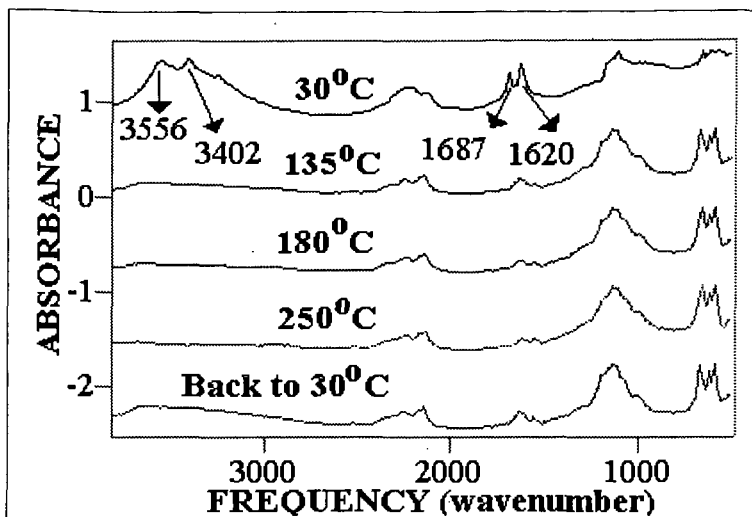


Fig. 3 This figure shows how temperature affected the diffuse reflectance-FTIR (DRIFT) spectrum of CWLP scrubber sludge.

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